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Microstructure of barium strontium titanate based glass-ceramics doped by Ce and La

A P Turygin¹, D S Chezganov¹, I S Baturin¹, X Song², Y Zhang² and V Ya Shur¹

¹School of Natural Sciences and Mathematics, Ural Federal University, 620000 Ekaterinburg, Russia

²Beijing Key Laboratory of Fine Ceramics, State Key Laboratory of New Ceramics and Fine Processing, Institute of Nuclear and New Energy Technology, Tsinghua University, 100084 Beijing, P.R. China

anton.turygin@urfu.ru

Abstract. The microstructure and surface morphology of $(\text{Ba}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ based glass-ceramics with different amounts of La and Ce were studied. It was shown that the addition of the 1.5% La and >2%Ce led to formation of dendrite-like structures. The isolated clusters of ferroelectric phase were found in all investigated samples. Fraction of ferroelectric phase was about 0.75% for La addition and 0.25% for Ce addition.

1. Introduction

Glass-ceramics representing ferroelectric grains embedded in a glass matrix are of significant interest for power electronic applications, especially for energy storage devices [1,2]. It has been shown that the application of the glass-ceramics based on the ferroelectric materials can improve energy storage properties by the utilization of a high dielectric constant of ferroelectrics and relatively high breakdown voltage of glass [2]. It is known that the aluminosilicate glass-ceramics based on $(\text{Ba},\text{Sr})\text{TiO}_3$ (BST) are among the most promising materials for the energy storage applications [3]. An addition of SrO is used for tuning the Curie temperature and increasing the dielectric constant at room temperature.

It has been shown that the energy storage properties of the BST glass-ceramics depend on their microstructure [4,5]. Different additives (AlF_3 , La_2O_5 , MnO_2 , etc.) were used to control the microstructure, thus optimizing the dielectric properties [5].

The effect of space charges (interfacial polarization) at the interphase boundaries between crystalline grains and glass on the breakdown voltage and the dielectric properties has been discussed [6-8]. At the same time, properties of the ferroelectric materials strongly depend on the domain structure, but little is known about the domain structure of the BST glass-ceramics. The purpose of the present paper is to study the microstructure of the BST glass-ceramics with different concentrations of La and Ce additives.

2. Experimental

The samples of BST based glass-ceramics with different concentrations of La and Ce additives were prepared from well-mixed powders by a melt technique. The glass samples with La addition have the composition of $m\text{BaO}-n\text{SrO}-29\text{TiO}_2-22\text{SiO}_2-12\text{Al}_2\text{O}_3-2.4\text{BaF}_2-x\text{La}_2\text{O}_3$ ($x=0, 0.5, 1.0$, and 1.5 mol%, $m=4n$, $m+n+x=34.6$ mol%) (BST-La x %). The ball-milled wet powder was melted in a platinum crucible at 1550°C for 4 h and then poured rapidly into a container filled with distilled water to obtain glass frits. The glass frits were subsequently ball-milled for 4 h to produce glass powder. This glass powder was



mixed with PVA and then pressed into small disk with 10 mm in diameter and 0.6 mm in thickness using uniaxial press. The pellets were heat-treated by two-step process for nucleation and subsequent crystal growth. The green pellets were first heated at 850°C for 1 h and then sintered at 950°C for 2 h to form the La-doped BST glass-ceramics. Glass samples with Ce addition have composition $m\text{BaO}-n\text{SrO}-29\text{TiO}_2-22\text{SiO}_2-12\text{Al}_2\text{O}_3-x\text{CeO}_2$ ($x = 0, 1, 2$, and 3 mol%, $m = 4n$, $m+n+x = 37$ mol%) (BST-Cex%). The powders were melted in a platinum crucible at 1550°C for 2-3 h and then poured rapidly into a container filled with distilled water to obtain glass frits. The glass frits were subsequently ball-milled for 4 h to produce glass powder. This glass powder was mixed with PVA and then pressed into small disks with 8 mm in diameter and 0.25 mm in thickness using uniaxial press. The pellets were heat-treated by two-step process for nucleation and subsequent crystal growth. The green pellets were first heated at 700°C for 4 h and then sintered at 950°C for 2 h to form the Ce-doped BST glass-ceramics.

The sample surface was polished by diamond paste with decreasing grain sizes from 6 to 0.25 μm . The final polishing was done by colloidal silica (SF1 Polishing Suspension, Logitech, UK). The sample thickness after polishing was about 200 μm .

The visualization of the domain structure with high spatial resolution was performed using piezoresponse force microscopy (PFM). The samples were mounted by conductive silver paste to the metal disks. PFM measurements were realized by a scanning probe microscope Asylum MFP-3D (Asylum Research, Oxford Instruments, UK). The silicon HA_{NC}/W2C tips (ScanSens, Russia) with a tungsten carbide conductive coating, radius of curvature $R = 35$ nm, resonance frequency $f = 380$ kHz, and spring constant $k = 35$ N/m were used. Piezoresponse measurements were realized by the application of 5 V AC far from the contact resonance frequency to the SPM tip.

The microstructure of the glass-ceramic samples was studied by a scanning electron microscope (SEM, Merlin, Carl Zeiss, Germany) with field-emission using secondary electron imaging with charge compensation.

3. Results and discussion

Investigation of the BST-La glass-ceramics microstructure by SEM demonstrated irregular-shaped grains with size below 100 nm for all samples (Fig. 1). It should be noted that the grain boundaries have low contrast, which makes it difficult to distinguish individual grains. All the grains can be separated by contrast in two groups: corresponding to glass matrix and ferroelectric phase (Fig. 1a-d). For structure analysis, auto-correlation function (ACF) technique can be used [6]. 2D ACF image is defined as:

$$C(r_1, r_2) = \sum_{x,y} D(x, y) \times D(x + r_1, y + r_2) \quad (1)$$

where $C(r_1, r_2)$ is an intensity of ACF in (r_1, r_2) point, $D(x, y)$ is an intensity of SEM image in (x, y) one.

SEM images (Fig. 1a-d) were analysed after binarization. Angle averaged profile of ACF image was fitted by function:

$$C(r) \sim \exp \left[- \left(\frac{r}{\xi} \right)^{2h} \right] \quad (2)$$

where r is the distance from the central maximum, $C(r)$ is ACF amplitude, ξ is the correlation radius, and h is a parameter.

Correlation radius for BST-La samples is about 55 nm for all samples and weakly depends on La concentration.

Formation of dendrite-like structures was found for high La concentration ($>1\%$) (Fig. 2a). The formation of dendrite structures in BST-based glass-ceramics with addition of AlF_3 , MnO_2 and rare earth elements were reported [1,7-11]. In general, the dendrites violate the uniform microstructure of ceramics, which leads to degradation of dielectric breakdown properties. However, such structures can increase dielectric permittivity due to large surface of phase boundaries.

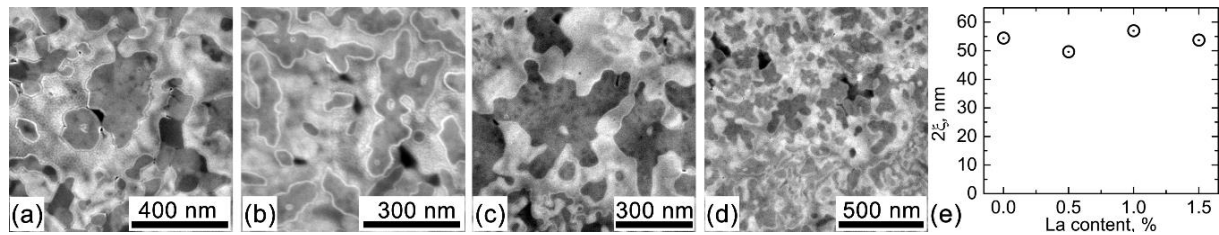


Figure 1. SEM images of BST-La glass-ceramics microstructure with various La concentration: (a) 0%, (b) 0.5%, (c) 1%, (d) 1.5%, (e) dependence of correlation radius on La content.

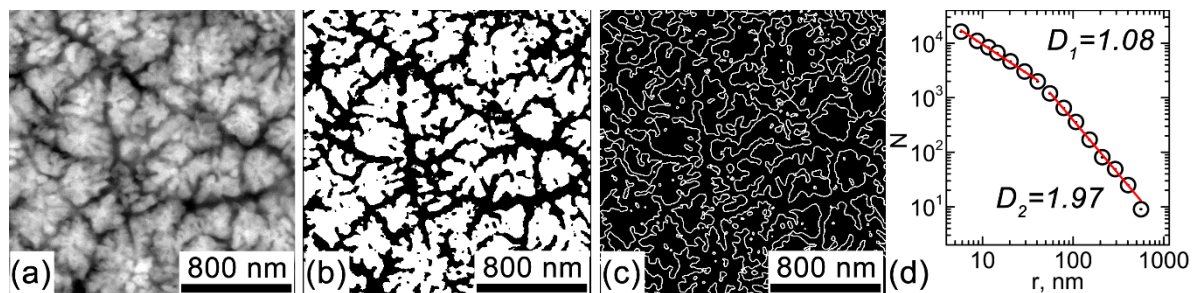


Figure 2. The dendrite structures in BST-La1.5%: (a) SEM image, (b) binarized image, (c) edge detected image, (d) dependence of box number on box size.

The analysis of fractal dimension of structure was done using box counting method after image binarization and edge detection (Fig. 2b,c). Two-level fractal structure was obtained (Fig. 2d) with fractal dimensions $D_1 = 1.08$ at scale below 100 nm and $D_2 = 1.97$ above 100 nm. Such large value of D_2 can indicate the compact dendrite structure [12]

Study of BST-Ce glass-ceramics did not reveal individual grains. The obtained microstructure slightly depended on Ce concentration (Fig. 3a-d). In the samples with Ce content below 2%, as-grown lamellar structures with period below 30 nm were found. Correlation radius decreased with increasing Ce content (Fig. 4e).

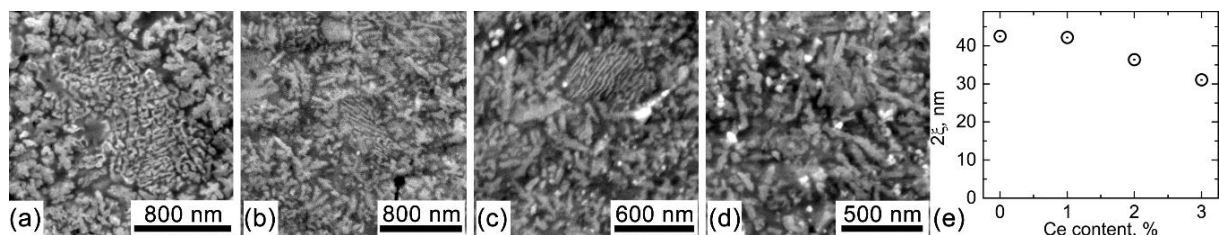


Figure 3. SEM images of BST-Ce glass-ceramics microstructure with various Ce concentrations: (a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) dependence of correlation radius on Ce content.

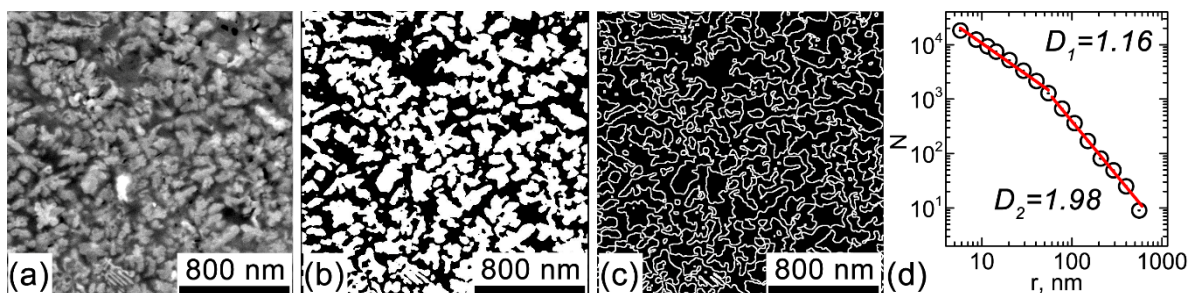


Figure 4. The dendrite structures in BST-Ce0%: (a) SEM image, (b) binarized image, (c) edge detected image, (d) dependence of box number on box size.

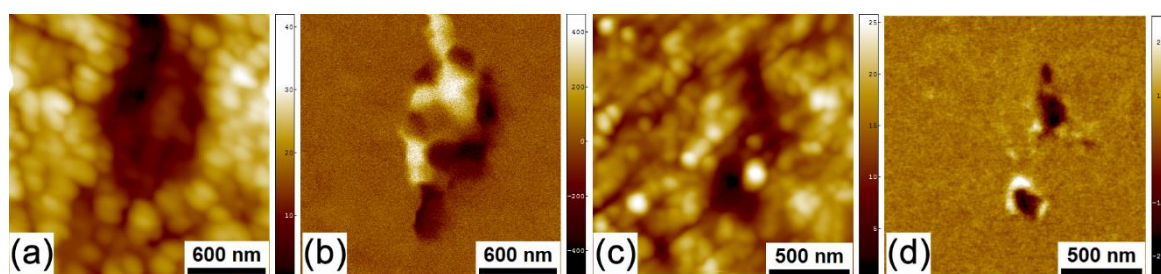


Figure 5. Domain structure in BST-La1%: (a) topography, (b) PFM image. Domain structure in BST-Ce2%: (c) topography, (d) PFM image.

In all BST-Ce samples, dendrite-like structures with size about several hundred nanometres were found (Fig. 3a-d). Application of box counting method for structure analysis (Fig. 4) allowed obtaining fractal dimension D_2 of about 1.98 for all BST-Ce samples, which indicates the compact structure.

In BST-La samples isolated clusters of polar phase with size from 0.2 to 3 μm were found by PFM (Fig. 5a,b). Fraction of polar phase was about 0.75% for all the samples and did not depend on La concentration. PFM studies in BST-Ce demonstrated presence of the same polar phase clusters with size from 0.2 to 1.5 μm and fraction about 0.25%, which was also independent on Ce concentration.

Application of the single voltage pulse to the tip with amplitude up to ± 200 V and duration 10 s did not allow obtaining local polarization reversal even at the elevated temperatures up to 90°C. This fact can be attributed to a strong clamping of the domain walls by glass matrix [13].

4. Conclusion

The microstructure and surface morphology of the BST glass-ceramics with La and Ce additions were studied. It was found that the addition of 1.5% of La led to formation of the compact dendrite structure. Ceramics with Ce addition possessed dendrite-like structures, decreasing in size with Ce concentration. Fraction of ferroelectric phase is below 1% in all the studied samples. The obtained information about microstructure can be used for further improvement of the dielectric properties of BST glass-ceramics.

Acknowledgements

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